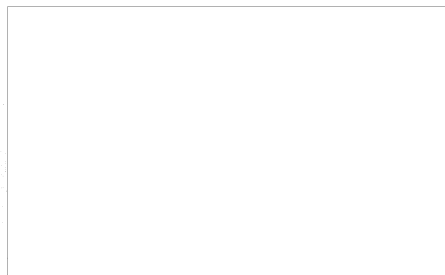


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Theory of Liquid Helium-3

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"Theory of Liquid Helium-3"

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[Abstract by the author]

In section 1 we determine the temperature dependence of thermal capacity, viscosity and thermoconductivity of He^3 . In section 2 we expound the influence of exchange effects produced by the nuclear spin of He^3 atoms on the phase transition of the liquid He^3 into solid state. The heat of fusion of He^3 at low temperatures should be negative and equal $-R \cdot \ln 2$. The possibility, in principle, to obtain temperatures of the order of 10^{-6} to 10^{-7}° during adiabatic solidification of liquid He^3 is indicated. Some peculiarities of nuclear magnetic susceptibility are explained.

* * * * *

[Text]1. THERMAL CAPACITY, VISCOSITY AND THERMAL CONDUCTIVITY OF He^3

It was recently established that liquid He^3 , unlike liquid He^4 , possesses no superfluidity down to the temperature of 1.05°K [1]. This result makes probable the assumption that He^3 does not reveal superfluidity at any temperatures. In the case of He^4 , Bose-Einstein statistics contribute to superfluidity [2]. But if we consider a gas sufficiently rarefied and subject to Fermi-Dirac statistics, then we may explain by the methods of perturbation theory the effect of interacting atoms on the properties of such a gas. The theory of perturbations appears to be applicable in the case of sufficiently low gas densities and in the case of short acting

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forces. Such computations do not reveal any superfluidity. In similar conditions a Bose gas in some cases reveals superfluidity [2]. Therefore there are some reasons to consider liquid He^3 non-superfluid. The energy of the excited state of He^3 for small exciting energies represents the sum of energies of elementary excitations of "quasi-particles" [3]. It is natural to consider such excitations as obeying Fermi-Dirac statistics, because in this case such excitations of the whole system pass in a continuous way into excited states in the sense of a progressive motion of separate atoms of He^3 , during the transition from liquid to gas. The properties of excitation of conducting electrons within metals lead to the same considerations of excitations as in liquid He^3 . As is known, the electron heat capacity in metals and a number of other properties correspond to Fermi-Dirac statistics of excitations. (The existence of superfluidity is due to some small effects not accounted for in the rough model of Fermi-Dirac. The smallness of these effects appears in the low temperatures at which the superfluidity appears, low in comparison with "natural" electron temperatures having the order of magnitude of degeneration of electrons.)

One case [4] is known, where the excitation of the system of interacting electrons obey Bose statistics. This case corresponds to states that differ little from the "zero" state in which all electron spins are oriented in one direction. Such a "zero" state is a "singular point," and therefore excitations in the vicinity of such a state also possess exceptional properties. In the case of liquid He^3 , as well as in the case of nonferrous metals in the non-superconducting state, the lowest "zero" state is characterized only by lowest energy and nothing else. (In the case of ferromagnetism it is characterized by a still higher magnetic moment). Because the wavelength of He^3 atoms is of the order of their mutual distance, the interaction of He^3 atoms does not depend on the mutual orientation of nuclear spins (the nuclear spin of He^3 equals $1/2$) [5]. Therefore the essential role in liquid He^3 is played by exchange effects, connected with the exchange of two He^3 atoms. It is

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easy to show that these exchange effects probably lead to a predominantly antiparallel orientation of adjacent nuclear spins; thus liquid He^3 is not a nuclear ferromagnetic, but represents an example of a nuclear exchange paramagnetic, similar to an electronic exchange paramagnetic of the solid oxygen type. Indeed, in the case of two He^3 atoms having parallel spins, the coordinate part of the wave function should be antisymmetrical relative to the permutation of two atoms. Therefore it cannot contain the function S . Under these conditions the probability of small distances between the He^3 atoms is not much probable in comparison with the case where the coordinate part of the wave function of two atoms may contain the S function; i.e., when the spins are antiparallel. If we take into account the rapid decrease in negative attraction between two atoms He^3 with increase of their mutual distance, we come to the conclusion that the energy of two He^3 atoms will be lower in the case where they can rather approach each other; i.e., in the case of antiparallel orientation of adjacent spins. Although in this case we are discussing small distances between atoms, they are however greater than r_0 , where r_0 is the distance at which intensive repulsion begins. This limitation holds well in the case of liquid He^3 , because the average distance between atoms is a several times greater than r_0 . This is just the reason for the existence of liquid He^3 in which the atoms on the average are attracted to each other. Therefore we have no reasons to consider liquid He^3 a nuclear ferromagnetic. Hence we may assume that near the zero state of He^3 the statistics of excitations coincides with the statistics of atoms.

Using the Fermi-Dirac distribution for excited states, we may easily derive a number of conclusions concerning some properties of liquid He^3 . The Fermi surface in the considered case consists of a sphere of radius p_0 where p_0 is of the order of the magnitude $(3\pi^2)^{1/3} \hbar N^{1/3}$ (N is the number of atoms per cm^3 ; it was taken into account here that the nuclear spin of He^3 equals $1/2$.) At temperatures small in

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comparison with the temperature of degeneration, excitations will have momenta approaching p_0 in magnitude. Expanding the excitation energy ϵ in a series in powers of $(p - p_0)$, we obtain

$$\epsilon = v |p - p_0| \quad (1)$$

Because at a temperature T the main role belongs to excitations at which $\epsilon \sim T$, and the number of such excitations (per cm^3) equals $p_0^2 \Delta p / \pi^2 \hbar^3 \sim p_0^2 \epsilon / \hbar^3 v \sim p_0^2 T / \hbar^3 v$, then the energy per cm^3 of He^3 depends on the temperature in the following way:

$$u = u_0 + (1/2) a T^2 \quad (2)$$

$$a = \gamma p_0^2 / \hbar^3 v; \quad \gamma \sim \pi^{-2} \quad (3)$$

Relations (1) and (2) are correct at temperatures sufficiently small in comparison with the temperature T_0 of degeneration of excitations. This temperature is of the order of magnitude 5° :

$$T_0 \sim p_0^2 / 2m \sim (3\pi^2)^{2/3} \hbar^2 N^{2/3} / 2m \sim 5^\circ$$

According to expression (2) the heat capacity of He^3 appears to be proportional to temperature:

$$c = aT \quad (T \ll T_0) \quad (4)$$

This conclusion enables us experimentally to directly check the Fermi character of the energy spectrum. It is easy to establish the temperature dependence of some kinetic characteristics of He^3 . For this purpose let us determine the length of free path of excitations. The free path of excitations is terminated by mutual collisions. The amount of excitations per cm^3 is of the order of magnitude of N :

$$n \sim p_0^2 \Delta p / \hbar^3 \sim p_0^2 T / \hbar^3 v \sim NT / T_0 \ll N \quad (5)$$

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Because $n \ll N$, even collisions are the most probable. For each collision of two excitements, both states obtained after collisions should have momenta near p_0 . This decreases the effective cross-section of such collision, because the probability of collisions is proportional to the number of possible final states. The number of states after collision equals

$$\frac{dk d\Omega}{(2\pi\hbar)^3} = \frac{k^2 dk d\Omega}{(2\pi\hbar)^3} \Omega = \frac{p_0^2 d\Omega d\Omega}{(2\pi\hbar)^3} \quad (6)$$

k is the momentum of one particle after collision, and $d\Omega$ is an element of the solid angle characterizing the direction of propagation of the particle. During integration, over $d\Omega$, a factor proportional to temperature appears. Hence the effective cross-section σ for the collision of two excitements appears to be of the order of

$$\sigma = \sigma_0 \frac{T}{T_0} \quad (7)$$

where σ_0 has an order of magnitude of the gas kinetic cross-section (10^{-15} cm^2). By combining (5) and (7) we find the length of free path of the excitement

$$l \sim \frac{1}{N\sigma_0} \left(\frac{T_0}{T} \right)^2 \quad (8)$$

a result obtained previously during discussion of free path of electrons in metals, due to interaction of electrons [5, 7] (see also [8]).

The found length of free path allows one to establish the temperature dependence of the viscosity of liquid He^3 , because all kinetic properties of He^3 may be found in a discussion of a gas of excitations with properties described in relations (1) to (8). Because $\eta = l N m \cdot v$, then by substituting (8) we find

$$\eta = N m \frac{1}{N\sigma_0} \left(\frac{T_0}{T} \right)^2 v = \frac{A}{T^2} \quad (9)$$

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The viscosity of liquid He^3 should be inversely proportional to the square of the temperature at $T \ll T_0$.

With help of (8) and (4) we obtain the thermal conductivity of liquid He^3 ,

$$\kappa = \frac{1}{2} c v = B/T \quad (10)$$

The thermal conductivity of liquid He^3 should be inversely proportional to the absolute temperature at $T \ll T_0$.

The formulas (4), (9) and (10) enable us to experimentally check the expounded theory. We should remark once more that in the derivation of relations (4), (9), and (1) we did not use the model of an ideal gas in the application to ~~some~~ He^3 atoms.

2. INFLUENCE OF EXCHANGE EFFECTS IN LIQUID He^3 ON PHASE TRANSITION OF LIQUID He^3 TO SOLID He^3

Although as of now solid He^3 has not yet been obtained, it is doubtless that, under a pressure of the same order as that in the case of He^4 , liquid He^3 will solidify. The reason for solidification under strong pressure consists in the fact that with decreasing volume (under action of applied pressure) the ratio of amplitude of zero oscillations to interatomic distance decreases. If at low pressures (large volumes) this ratio in the case of liquid He^4 and He^3 appears to be of the order of unity (which hinders solidification) then with decrease of volume this ratio becomes smaller than unity, and therefore the formation of crystals becomes possible. (introduced by L.D. Landau) let us compare the amplitude of zero oscillations In order to prove the above expounded considerations $\sqrt{\hbar/m\omega}$ with the inter-atomic distance b . By (1) we should understand some average frequency connected to the potential energy of interaction of two atoms in the following way:

$$m\omega^2 \approx (d^2u/dr^2)_{r=b}$$

Assuming $u = \alpha/r^n$, where $n \sim 6-8$ [9], we obtain

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$$\sqrt{\frac{\pi}{m\omega}} \cdot \frac{1}{b} \sim \left(\frac{\pi}{m\omega}\right)^{\frac{1}{2}} b^{(n-2)/4} \xrightarrow{b \rightarrow 0} 0,$$

in view of $n \gg 2$.

It is easy to show that the phase transition: liquid He^3 -- solid He^3 should reveal some special peculiarities produced by exchange effects of He^3 atoms in the liquid state. For the clarification of these peculiarities, let us compare the entropy S of the liquid and solid phases in He^3 . In the liquid state, S tends to zero as temperature drops to zero. If the Fermi-Dirac distribution of excitations is correct, then S should be proportional to T [10]. We should, however, note that the matter of what kind of function S in liquid state is of T is not essential for further discussion. The only important fact is the decrease of S with decreasing T . It is also important to emphasize here that that part of S produced by nuclear spins also drops. In the case of the absence of exchange effects due to nuclear spin, the spins of nuclei would be free in spatial orientation down to temperatures so low that the magnetic interaction of nuclear spins with each other would become essential. These temperatures have a magnitude of the order of 10^{-7}° ;

$$T_M \sim \frac{\mu^2}{kb^3} \sim 10^{-7}^\circ, \quad \mu \sim 10^{-23} \quad (11)$$

Therefore in the case of the absence of exchange effects at $T \gg T_M$, a term equal to $R \cdot \ln 2$ (per gram-atom) would make up part of S . Exchange effects cause the appearance of a correlation among the orientations of spins of adjacent He^3 nuclei already at temperatures of the order of degrees; i.e., "natural" helium temperatures. This conclusion follows from the fact that the difference in energy of interaction of two He^3 atoms in the case of parallel or antiparallel orientation of spins is of the same order as the energy of interaction itself (see section 1). In this case it is

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of no importance whether He^3 is a liquid exchange nuclear paramagnetic or ferromagnetic. The character of correlation in these two cases is different, but the very existence of correlation should occur in each of these cases at $T \lesssim 1^\circ$. It follows from this that the part of S produced by nuclear spins drops to values smaller than $R \cdot \ln 2$ already at $T \lesssim 1^\circ$. Because entropy not bound to nuclear spin also drops, then already at $T \lesssim 1^\circ$, the whole entropy of liquid He^3 should drop to values below $R \cdot \ln 2$. Let us now compare this entropy with the entropy of solid He^3 . The existence of a crystalline lattice, in which the amplitude of zero oscillations is much smaller than the interatomic distance, leads either to the vanishing of effects connected with exchange of two atoms, or to considerable decrease of such effects. Therefore in solid He^3 nuclear spins should have free orientation up to $T \sim T_M$. Therefore the entropy of solid He^3 possesses a part equal to $R \cdot \ln 2$, if $T \gg 10^{-7}^\circ$. Because the part of S due to oscillations is proportional to T^3 and is of the order of magnitude of $(12/5)\pi^4 R (T/\theta)^3$ ($\theta \gtrsim 30^\circ$), the entire entropy of solid He^3 at $T \lesssim 1^\circ$ appears to be constant and equal to $R \cdot \ln 2$. (NOTE: θ of liquid He^4 equals 30° [cf 11]; θ of solid He^3 must be of the same order of magnitude.) Only in the case of $T \lesssim T_M$ does the magnetic interaction of nuclear spins in the crystal decrease S rapidly to zero at $T \ll T_M$. An example of the dependence of S on T in two phases of He^3 is represented in figure 1. Note that $T_1 \sim 1^\circ$. We see that, at temperatures T such that

$$10^{-7}^\circ \sim T_M \ll T \ll T_1 \sim 1^\circ,$$

the entropy of solid He^3 appears to be higher than in the liquid phase; i.e., it brings about a correlation, as opposite to usual. Therefore during an isothermal transition of solid He^3 to liquid He^3 heat should not be absorbed but emitted; and vice-versa; during isothermal solidification heat should be absorbed. We deal here with negative heat of fusion Q , the value of which equals at $T_M \ll T \ll T_1$

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$$Q = T(S_{liq} - S_{sol}) = -RT \ln 2 \quad (12)$$

At the same temperatures a peculiar dependence of pressure on temperature obtains, at which phase transition occurs. According to the Clausius-Clapeyron relation

$$dp/dT = (S_{sol} - S_{liq}) (v_{sol} - v_{liq}),$$

we have

$$dp/dT = R \ln 2 / (v_{sol} - v_{liq}) = -R \ln 2 / (v_{liq} - v_{sol}) < 0 \quad (13)$$

It is assumed here that the liquid has a bigger volume than the crystal.

Starting with certain temperatures of the order of degrees, S_{liq} will be bigger than S_{sol} . Therefore p as a function of T has the form represented in figure 2. The existence of a rectilinear portion with negative slope at low temperatures qualitatively distinguish He^3 from He^4 , in which portion the dependence of p on T possesses quite a different character [12] (figure 3).

Notice that at $T \ll T_M$, S_{sol} tends to zero, due to the occurring correlation among the spins in the crystal. Here dp/dT tends to zero. If we consider the adiabatic solidification of He^3 , then as seen from figure 1 the possibility of obtaining solid He^3 at extremely low temperatures of the order of 10^{-6} to $10^{-7}K$ seems evident. In order to achieve it, it is necessary to compress adiabatically liquid He^3 having a temperature below T_1 to a pressure at which solidification occurs.

The condition of equality of entropy in the solid and liquid state will produce in the crystal a temperature of the order of T_M (the transition occurs along the dotted line in figure 1).

The application of thermodynamic correlations to the phase transition of liquid He^3 to the solid state assumes that all the corresponding relaxation periods are small. Clarification of the realization of this assumption requires a particular discussion.

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The exchange effects in liquid He^3 should also influence the nuclear magnetism of He^3 , because the free orientation of nuclear spins stops not at $T \sim T_M$, as in most other bodies (except compounds of the type of ortho- or parahydrogen), but at $T \sim 1^\circ$. Beginning with these temperatures the nuclear magnetic moment of liquid He^3 in an external magnetic field should not be inversely proportional to temperature $[13]$, but should depend on temperature in the same way as the susceptibility of exchange electrons of paramagnetics of the solid oxygen type. In the liquid He^3 model discussed in section 1, the nuclear magnetic susceptibility of He^3 should be independent of temperature at $T \lesssim 1^\circ$.

Finally I should like to thank Acad L. D. Landau for his valuable counsel and constant attention paid to my work, and also V. V. Vladimirovskiy for his interesting discussion of certain topics of my work.

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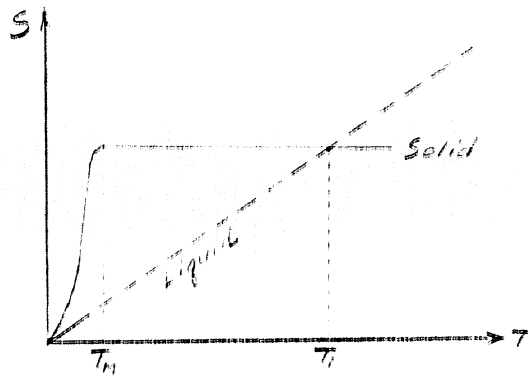


Figure 1.

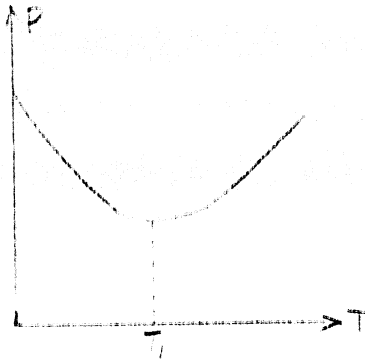


Figure 2.

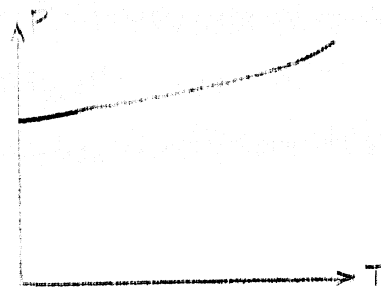


Figure 3.

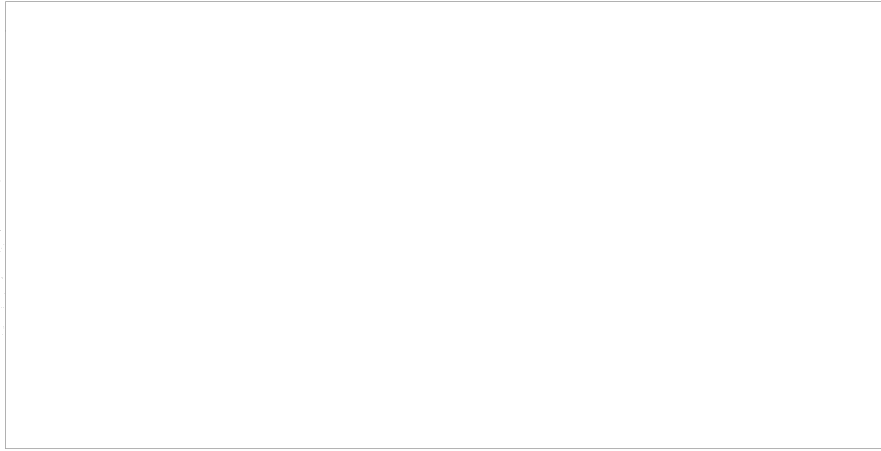
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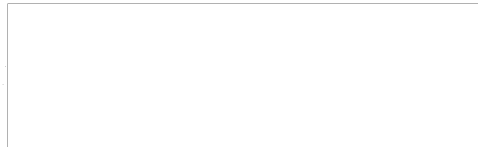
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N-OXIDES OF ALKALOIDS IN PLANTS

M. P. Kir'yakov

In recent years, investigations by Russian and foreign workers established that N-oxides of alkaloids occur rather extensively in plants side-by-side with the reduced form. While some of the N-oxides are of practical importance, their value also lies in the fact that phyto-biochemical conditions can be observed by detecting them and determining their content. Thus, G. P. Men'shikov and G. I. Borodina established that the total quantity of alkaloids in *Trachelanthus Kerolkevi* amounts to 2.5% in May, 90% of this quantity being trachelantaxine N-oxide. In July the total content of alkaloids in this plant drops to 0.4%, but the alkaloids are 100% reduced (i.e., to the form of trachelantaxine).

In determining the quantitative changes of the alkaloid N-oxide content in the case of *Semecio platyphyllum*, L. Ya. Arushkina obtained the values listed in the attached table. Changes in the composition of the alkaloids take place in the leaves of the plant as well as in the rhizome at the expense of N-oxides, with the difference that in the leaves there is reduction of the quantity of N-oxides, while this quantity increases in the rhizome and reaches as much as 3.8% towards the end of the vegetation period of the plant. When the rhizome enters the period of dormancy, N-oxides disappear and the content of reduced alkaloids in it reaches 2.74%. The quantity of reduced alkaloids during the growth period of *Semecio platyphyllum* is small and does not vary much in comparison with that of N-oxides.

The facts outlined above suggest that alkaloids are not merely waste matter (as formed as an end product in the plant's metabolism, but fulfill an essential physiological function.

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Content of Alkaloids in Various Parts of *Semecle platyphyllos* During Different Periods of the Plant's Life
(% referred to dry weight)

Phase of development	Rhizome		Organs and parts of the plant		Stalks	Buds	Flowers	Seeds
	N-oxides	Reduced alkaloids	N-oxides	Reduced alkaloids				
Germination	1.89	0.32	2.94	0.22	1.18	-	-	-
Seedling	2.50	0.25	2.47	0.21	0.76	5.36	-	-
Flowering	3.34	0.22	1.09	0.11	-	-	3.35	-
Ripening of seeds	3.80	0.26	0.39	0.10	0.18	-	-	4.62
Dormancy	Absent	2.74						

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